Coagulation and flocculation







Framework

This module represents coagulation and flocculation.

Contents

This module has the following contents:

- 1. Introduction
- 2. Coagulation
 - 2.1 Theory of coagulation
 - 2.2 Coagulation in practice
- 3. Flocculation
 - 3.1 Theory of floc formation
 - 3.2 Floc formation in practice

1 Introduction

In surface water different compounds are present that must be removed if drinking water is to be produced. The compounds can be subdivided into:

- suspended solids
- colloidal solids
- dissolved solids.

Suspended solids have a diameter larger than 10^{-6} m, colloidal solids between 10^{-9} and 10^{-6} m and dissolved solids smaller than 10^{-9} m.

Particles with a diameter larger than 10⁻⁵ m, and a specific density larger than 2,000 kg/m³ will settle in water. Smaller particles will also settle, but more slowly.

In Table 1 the settling time of particles with a density of 2,650 kg/m³ (e.g., sand) is given.

To be removed, particles that are smaller than 10⁻⁵ m must be made larger or heavier. The latter is impossible and, therefore, removal is only possible by increasing the particle size.

During the coagulation process, coagulants are added to the water to aid in floc formation. These flocs are precipitates in water, wherein small particles are incorporated.

To express the concentration of compounds in water, sum parameters are used. The most important sum parameters for surface water are "suspended solids" concentration (dry weight), "turbidity," "natural organic matter" (expressed in TOC/DOC) and "color."

"Suspended solids" concentration and turbidity

Table 1 - Settling time of particles with a density of 2,650 kg/m³

Diameter (m)	Types of particles	Settling time over 30 cm
10 ⁻²	gravel	0.3 sec
10 ⁻³	coarse sand	3 sec
10 ⁻⁴	fine sand	38 sec
10 ⁻⁵	silt	33 min
10 ⁻⁶	bacteria	35 hours
10 ⁻⁷	clay	230 days
10 ⁻⁸	colloids	63 years



Figure 1 - Turbidity in surface water

(Figure 1) are caused by colloidal particles (order of magnitude $0.1 - 10 \mu m$). Colloidal particles are negatively charged and repulse each other.

In the tropics high concentrations of suspended solids can occur and rivers can be become "mud flows" (Figure 2).

Color (Figure 3) is caused by humic substances (order of magnitude 0.01 μ m). The charge of humic substances (and thus the removal) is dependent upon the pH of the water.

In Table 2 the water quality data from the surface water of several rivers in the Netherlands and in tropical countries are given. The high values of organic matter and color in the Drentsche Aa are caused by peat-containing soils (with high organic matter content) that the river crosses.

2 Coagulation

The coagulation process is the dosing of a co-



Figure 2 - Rivers in the tropics sometimes have high suspended solids contents



Figure 3 - Color in water

agulant in water, resulting in the destabilization of negatively charged particles.

2.1 Theory of coagulation

Coagulants

To remove particles present in water, the particles must be incorporated into flocs. These flocs will be formed after dosing coagulant.

In the Netherlands iron chloride (FeCl₃) is frequently used as the coagulant. Alternatively, aluminum sulfate $(Al_2(SO_4)_3)$ can be applied.

Iron

Iron chloride is easy to dissolve in water; the solubility product (K_{sp}) is 27.9 mol⁴·l⁻⁴. Consequently, 162 mg FeCl₃ can be dissolved in one liter of water, resulting in 55.8 mg/l Fe³⁺ and 106.5 mg/l Cl⁻.

In addition to other ions, the ions Cl^{-} , SO_4^{2-} , Na^+ , Ca^{2+} , H_3O^+ - and OH^- are dissolved in water. The OH^- ions play an important role in coagulation. Fe³⁺- and OH^- ions precipitate, because the solubility product of iron hydroxide is low. Since $K_{sp Fe(OH)3} = 1 \cdot 10^{-38} \text{ mol}^{4} \cdot l^{4}$, only $7.8 \cdot 10^{-10} \text{ mol/l}$ Fe³⁺ and $2.34 \cdot 10^{-9} \text{ mol/l}$ OH⁻-ions can be present in water.

When the concentration of these ions is higher, they will precipitate into $Fe(OH)_3$ -flocs.

When the pH of the surface water is known, the concentration of iron (Fe^{3+}) ions can be calculated using the solubility product of iron hydroxide and the ion product of water:

$$\begin{split} &\mathsf{F}e^{3^{+}} + 3 \cdot \mathsf{O}H^{-} \to \mathsf{F}e(\mathsf{OH})_{3} \quad \mathsf{K}_{\mathsf{sp}} = 1 \cdot 10^{-38} \\ &2 \cdot \mathsf{H}_{2}\mathsf{O} \rightleftarrows \mathsf{H}_{3}\mathsf{O}^{+} + \mathsf{O}H^{-} \qquad \mathsf{K}_{\mathsf{w}} = 1 \cdot 10^{-14} \end{split}$$

Rewriting the water equilibrium results in the following equation:

$$K_{w} = 1 \cdot 10^{-14} = [H_{3}O^{+}] \cdot [OH^{-}] \Longrightarrow [OH^{-}] = \frac{1 \cdot 10^{-14}}{[H_{3}O^{+}]}$$

Combining the equation mentioned above with the solubility product of iron hydroxide gives:

$$\begin{split} & [Fe^{3+}] \cdot [OH^-]^3 = 1 \cdot 10^{-38} \Longrightarrow \\ & [Fe^{3+}] = 1 \cdot 10^{-38} \frac{[H_3O^+]^3}{(1 \cdot 10^{-14})^3} = 1 \cdot 10^4 \cdot [H_3O^+]^3 \\ & \log[Fe^{3+}] = \log(1 \cdot 10^4) + 3 \cdot \log[H_3O^+] = 4 - 3 \cdot pH \end{split}$$

In addition to iron hydroxide the following hydrolyses products of Fe³⁺ are also formed:

Fe(OH)²⁺, Fe(OH)₂⁺, Fe(OH)₄⁻.

In Table 3 the solubility constants of different reactions are given. From here, after some calculation, Figure 4 can be constructed.

	Table	2 -	Water	quality	data	of several	rivers
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Disco	Over a start of a still de	To call 1 all to a	Oslan	500
River	Suspended solids (mg/l)	(NTK)	(mg Pt/l)	(mg/l)
Rhine	9 - 53	5.5 - 22.5	9 - 17	3.1 - 6
Meuse	4 - 31	2.2 - 27	10 - 22	3.4 - 5.4
Biesbosch reservoirs	1.5 - 9	0.9 - 5.6	6 - 12	3.2 - 4.0
IJsselmeer	4 - 115	2.5 - 4.0	10 - 30	5 - 13.3
Drentsche Aa	2 - 20	3.4 - 39	10 - 100	4.8 - 14.9
Tropical river	10,000	5,000	1,000	500
Drinking water	< 0.05	< 0.1	< 20	1

Table 3 - Iron hydrolyses reactions

Iron hydrolyses reactions				Ks
	Fe(OH) ₃	\leftrightarrow	Fe ³⁺ + 3OH-	1·10 ⁻³⁸
	Fe ³⁺ + 2H ₂ O	\leftrightarrow	$Fe(OH)^{2^+} + H_3O^+$	6.8·10 ⁻³
	$Fe(OH)^{2+} + H_3O^+$	\leftrightarrow	Fe(OH) ₂ ⁺ + H ₃ O ⁺	2.6·10 ⁻⁵
	2Fe ³⁺ + 4H ₂ O	\leftrightarrow	Fe ₂ (OH) ₂ ⁴⁺ + 2H ₃ O ⁺	1.4·10 ⁻³
	Fe(OH) ₃ + OH-	\leftrightarrow	Fe(OH) ₄ ⁻	1.0·10 ⁻⁵

When the pH of water is known, the amount of hydrolysis product in a volume of water can be determined. With a pH of 4.6, 10^{-7} mol/m³ Fe³⁺, 10^{-4} mol/m³ FeOH²⁺ and 10^{-4} mol/m³ FeOH₂⁺ are present.

The pH and the predominant hydrolysis product influence the predominant coagulation mechanisms.

As a result of the dosing of iron chloride, OH ions are removed and the pH will decrease.

The magnitude of the pH drop depends on the buffering capacity of the water. The higher the buffering capacity, the smaller the pH drop is. When the pH drop is too large, pH will be increased by dosing a base, such as caustic soda.

Alumn

Aluminum sulfate (alumn) is easy to dissolve in water and Al^{3+} en SO_4^{2-} ions will form. $Al(OH)_3$ has a low solubility product and precipitates.

By dissolving aluminum sulfate, different hydrolyses products are formed and, after calculating the solubility products, Figure 5 can be drawn.

Coagulation mechanisms

Destabilization of turbidity and color-causing



Figure 4 - Forms of iron hydrolyses products



Figure 5 - Forms of aluminum hydrolyses products

substances can be induced by different mechanisms.

The following subdivisions can be made:

- electrostatic coagulation
- adsorptive coagulation
- precipitation coagulation.

Electrostatic coagulation

In electrostatic coagulation, positively charged ions approach the negatively charged colloids. In the diffusive layer around the colloid, the positively charged ions accumulate, destabilizing the colloid.

In Figure 6 the mechanism of electrostatic coagulation is represented.

In the left part of the figure the negatively charged colloids are shown. After dosing coagulant (right part of the figure), the exterior of the colloidal particle is destabilized and can collide with other particles forming removable flocs.

Electrostatic coagulation occurs after dosing 0.025 mol/m³ of trivalent ions. These concentrations are not found in surface water treatment and thus elec-



Figure 6 - Mechanism of electrostatic coagulation

COAGULATION AND FLOCCULATION

WATER TREATMENT



Figure 7 - Mechanism of adsorptive coagulation

trostatic coagulation does not play an important role in water treatment.

Adsorptive coagulation

In adsorptive coagulation, particles are adsorbed to the positively charged hydrolyses products FeOH²⁺ and FeOH²⁺.

These products mainly occur at low pH (Figure 4). The optimal pH-range for adsorptive coagulation with iron salts is between 6 and 8; the optimal pH-range with aluminum salts is narrower and is about 7.

Characteristics of adsorptive coagulation are that dosing is proportional to the removal of organic matter and that restabilization can occur after an overdose of coagulant. After an overdose, the colloids will be positively charged and repulsion of the particles will take place.

Adsorptive coagulation is a rapid process. Within one second, positively charged hydrolyses products are formed and are adsorbed to the negatively charged particles.

Precipitation coagulation

In precipitation coagulation, or sweep coagulation, colloids are incorporated into neutral (iron) hydroxide flocs. This mechanism occurs mainly in waters with low suspended solids content (10 mg/l). In order to form hydroxide flocs, more coagulant must be dosed than is necessary for adsorptive coagulation.



Figure 8 - Mechanism of precipitation coagulation



Figure 9 - Jar-test apparatus

2.2 Coagulation in practice

Jar test

The coagulation process can be researched by executing jar tests. In this test the coagulation and floc formation process is simulated.

The jar-test apparatus consists of 6 jars filled with water (Figure 9). To each jar a certain dose of coagulant is added. After rapid mixing, a slow stirring, and a settling phase, the water turbidity is measured.

By modifying the process conditions (dosage, pH, flocculation time, settling time, stirring energy for mixing and/or flocculation), the optimal conditions can be determined.

Mechanisms

The coagulation mechanisms discussed above occur in practice in parallel. This can be illustrated by discussing the results of several jar-test experiments.



Figure 10 - Results of jar-test experiment with varying coagulant dosing

WATER TREATMENT



Figure 11 - Influence of coagulant dose (left: high dose, right: low dose)

In Figure 10 the results of a jar-test experiment of Biesbosch water is shown. Biesbosch water originates from the river Meuse and is collected in reservoirs. Due to the long retention times (about 6 months) in the reservoirs, the suspended solids concentration of Biesbosch water is low, about 5 mg/l.

It can be concluded from the figure that turbidity decreases with an increased coagulant dosing. The lowest turbidity is attained when about 12 mg/l iron chloride is dosed. With a higher dosage the turbidity does not increase and thus restabilization does not occur.

In Figure 12 a coagulant dose of 12 mg/l and a varying pH is represented. The turbidity increases with a decreasing pH (pH<7).

The predominant coagulation mechanism of Biesbosch water is precipitation coagulation.



In the province of Zeeland in the Netherlands, the

Figure 12 - Results of jar-test experiment with varying pH



Figure 13 - Results of jar-test experiment of "polder water" with varying pH

drinking water company takes its water in from a polder as its source for the water treatment. Polder water has a high content of organic matter (like humic acids).

In Figure 13 the results are represented for jar-test experiments in which the coagulant dose varied with pH. At pH between 6 and 7 the lowest turbidity is found. At higher pH the turbidity is higher.

The prevailing mechanism is thus adsorptive coagulation.

An evident difference between the adsorptive and precipitation mechanisms is encountered during the coagulation of water from the Rhine. The water transport company Rijn-Kennemerland abstracts raw water from the river at Nieuwegein (WRK I-II) and from the IJsselmeer (lake) at Andijk (WRK III).

Although both water sources originate in the river Rhine, the coagulation mechanisms differ strongly



Figure 14 - Coagulation of Rhine water

COAGULATION AND FLOCCULATION



Figure 15 - Rest turbidity at different G_c-values

(Figure 14). The river water has a higher turbidity than the lake water; the lake water has a higher humic acid content than the river water due to algae bloom in summer.

During coagulation of lake water, restabilization can occur and the prevailing mechanism is adsorptive coagulation.

Restabilization is not detected in the coagulating river water and, therefore, the prevailing mechanism is precipitation coagulation.

Mixing

Rapid mixing after coagulant dosing is an important design parameter. The coagulant must be uniformly mixed with the raw water. In case mixing is poor, local under- and overdosing occurs, resulting in poor performance of the process.

The parameter expressing mixing intensity is called the velocity gradient or G-value.

The velocity gradient is defined as follows:



Figure 16 - Mechanical mixers

$$G_c = \sqrt{\frac{P}{\mu \cdot V}}$$

in which:

G	=	velocity gradient for rapid mixing	(S ⁻¹)
Ρ	=	dissipated power	(W)
μ	=	dynamic water viscosity	(N·s/m²)
V	=	volume of mixing tank	(m³)

The influence of the velocity gradient can be determined by jar-test experiments (Figure 15). When the velocity gradient is low (less intensive mixing), the residual turbidity will be higher than in situations where the velocity gradient is high. In practice, the recommended G-value for rapid mixing is 1500 s⁻¹, at a minimum.

Two different mixing systems can be applied:

- mechanical mixing
- static mixing

In the first system mechanical mixers dissipate the power in the raw water, while in the second system gravity forces cause the mixing effect. Here, the dissipated power is a consequence of the head loss over the mixing tank:

$$\textbf{P} = \rho \cdot \textbf{g} \cdot \textbf{Q} \cdot \Delta \textbf{H}$$



Figure 17 - Cascade mixer

in which:

ρ	=	density of water	(kg/m³)
g	=	gravity constant	(m/s²)
Q	=	flow	(m³/s)
Δŀ	1=	head loss over mixing tank	(m)

The equation for the velocity gradient for static mixers can be written as:

$$G_{c} = \sqrt{\frac{\rho \cdot g \cdot \Delta H}{\mu \cdot \tau_{c}}}$$

in which:

 τ_{c} = residence time in the mixing zone (s)

The most frequently applied static mixer is the cascade. Water falls over a weir into a receiving body. In the turbulent space that is caused by the falling water, coagulant is dosed.

3 Flocculation

3.1 Theory of floc formation

After coagulation and the resulting destabilization of particles, the particles must collide. The collision of particles can take place under natural circumstances (perikinetic floc formation) or by dissipation of mixing energy (orthokinetic floc formation).

Perikinetic floc formation

During perikinetic floc formation, particles collide as a result of Brownian motion. Von Smoluchowski described the decrease in the total number of spherical particles as a function of time with the following equation:

$$-\frac{\mathrm{dn}}{\mathrm{dt}} = \alpha \cdot \frac{4 \cdot \mathbf{k} \cdot \mathbf{T}}{3 \cdot \mu} \cdot \mathbf{n}^2$$

in which:

n = total number of particles per unit water volume (m⁻³)

$$\alpha$$
 = collision efficiency (-)

Κ	=	Boltzmann constant	(J·K ⁻¹)
-			

T = absolute temperature (K)

Not every collision will result in attachment and therefore the collision efficiency is incorporated into the equation.

From experiments it can be concluded that perikinetic floc formation is a fast process but results in poor settling characteristics of the formed flocs.

Orthokinetic floc formation

By mixing, the collision frequency of the particles is artificially increased. The decrease **in** the total number of particles as a function of time is described by the following equation:

$$-\frac{\mathrm{d}n}{\mathrm{d}t} = \frac{4}{3} \cdot \alpha \cdot \mathbf{n}_1 \cdot \mathbf{n}_2 \cdot \mathbf{R}^3 \cdot \mathbf{G}_{\mathrm{v}}$$

in which:

G _v =	velocity gradient for floc formation	(S⁻¹)
n _	collicion rediuc	(100)

R = collision radius (m)

 $n_1 =$ number of particles with diameter d_1 (-)

 n_2 = number of particles with diameter d_2 (-)

The collision radius is defined by $0.5 \cdot (d_1 + d_2)$. Assuming that all particles have the same diameter, the equation can be rewritten as:

$$-\frac{dn}{dt} = \frac{4 \cdot \alpha \cdot n^2 \cdot d^3 \cdot G_v}{3}$$

For spherical particles the volumetric concentration is described as:

$$c_v = \frac{1}{6} \cdot \pi \cdot \mathbf{n} \cdot \mathbf{d}^3$$

Deriving n·d³ and substituting it:

$$-\frac{\mathrm{d}n}{\mathrm{d}t} = \frac{8 \cdot \alpha \cdot \mathbf{n} \cdot \mathbf{C}_{v} \cdot \mathbf{G}_{v}}{\pi}$$

resulting in a solution for plug flow:

flow parallel to stirring axis: no short circuit flow



if flow speed = 0.03 m/s, tip speed = 1 m/s then water speed -0.97 to 1.03 m/s $\,$



$$\frac{n}{n_{o}} = e^{-k_{a} \cdot c_{v} \cdot G_{v} \cdot t}$$

and for completely mixed systems:

$$\frac{n}{n_o} = \frac{1}{1 + k_a \cdot c_v \cdot G_v \cdot t}$$

With these equations it can be calculated that orthokinetic floc formation of particles with a diameter of 1 μ m only takes place when velocity gradients higher than 10 s⁻¹ are applied. Otherwise, perikinetic floc formation is predominant.



Figure 19 - Plug flow mixing systems for floc formation, mixer in line with water flow

3.2 Floc formation in practice

Parameters that are important to the design of a floc formation installation are the following:

- residence time T
- residence time distribution
- velocity gradient for floc formation G_v
- floc volume concentration c_v.

Residence time

Time is needed for the formation of removable flocs. The applied residence time varies between 500 and 3600 sec. On average the residence time for floc formation is about 30 minutes.

To determine the required residence time, jar-test experiments are carried out.

Residence time distribution

When water flows through a tank, the residence time of every droplet is different. For some droplets the residence time is longer and for others shorter than the average. The consequence is that, in practice, the floc formation process performs worse than can be expected, based on theory. In order to approach the perfect plug flow where every droplet has the same residence time, criteria are developed for the design of a floc formation chamber. A plug flow can be approached when the ratio between the length and width of a tank is at least equal to 3.

Mixers in floc formation chambers take care of the dispersion of energy and collision of the particles. It is, however, important that the mixers be in line with the flow direction (Figure 18).



Figure 20 - Mixing device

If the mixers are placed perpendicular to the flow direction, some water droplets are accelerated and other are slowed down, resulting in a larger residence time distribution.

When the axis of the mixer is in line with the flow, the influence is limited.

In two different floc formation systems the length/ width ratio of 3 and the direction of the mixers are considered:

- horizontal, long and narrow (Figure 19 right).
- vertical, deep and narrow chambers (Figure 19 left).

Velocity gradient

After coagulation the colloids and humic acid are destabilized and many small particles are present in the water.

Mixers that are placed in the floc formation chambers dissipate energy in the water (Figure 20), resulting in the collision of neutral particles and the formation of flocs.

The degree of energy dissipation is expressed, like for coagulation, in the velocity gradient. The velocity gradient is mainly created by mixers.

Alternatively, hydraulic floc formation can be applied where the head loss between two chambers delivers the energy for the formation of flocs. The drawback of hydraulic flocculation is the uneven energy input.

The velocity gradient for floc formation is expressed in the parameter G_v and is defined by:



Figure 21 - Tip velocity



Figure 22 - Floc formation installation WRK I/II

$$G_v = \sqrt{\frac{P}{\mu \cdot V}}$$

The energy dissipation from the mixers can be calculated with the following equation:

$$\mathsf{P} = \rho_{\mathsf{w}} \cdot \pi^3 \cdot (1 - \mathsf{k}_2)^3 \cdot \mathsf{N}^3 \cdot \sum (\mathsf{c}_{\mathsf{d}} \cdot \mathsf{L}_{\mathsf{blade}} \cdot (\mathsf{r}_{\mathsf{u}}^4 - \mathsf{r}_{\mathsf{i}}^4))$$

in which:

- $k_2 = \text{constant} \approx 0.25$ (-)
- N = rotation speed (rpm)

$$C_d = \text{constant} \approx 1.50$$
 (-)

$$L_{\text{blade}}$$
 = length of mixer blade (m)

- r_u = distance from exterior of mixing blade to axis (m)
- r_i = distance from interior of mixing blade to axis (m)

According to the formula for the dissipation energy from the mixer, the rotation speed is the only operation parameter. The other parameters are already determined during the design process. The velocity gradient in operation can thus be calculated by:

$$G_v = const. \cdot \sqrt{N^3}$$



Figure 23 - Floc formation installation WRK III, division in different compartments

COAGULATION AND FLOCCULATION

(TLV) Apping 5 4 3 2 1 0 5,5,5,5 20,20,10,10 40,20,10,5 80,40,10,5 G_v-value (s⁻¹)

Figure 24 - Influence of G-value on floc formation in different compartments

The calculated velocity gradient is the average in the floc formation chamber.

The velocity of the mixing blade in the floc formation chamber depends on the radius and the rotation speed. The velocity is greatest at the tip of the mixing blade and is called the tip velocity (Figure 21) and can be calculated by:

$v_{tip} = 2 \cdot \pi \cdot r \cdot N$

The higher the rotation speed, the higher the tip velocity. When the tip velocity is higher than 1 m/s, formed flocs are broken up.

When the rotation speed of a mixer is known, the maximum radius of a mixing blade can be determined. A rotation speed of 4 rotations per minute allows a maximum radius of 2.4 meters.

During coagulation small neutral particles are





Figure 26 - Floc blanket installation at Berenplaat

formed and grow, after collision, into removable flocs.

To increase the collision frequency of the particles, a high mixing intensity must be applied. The small particles collide and larger particles are formed, but in the mean time, the risk of floc break-up increases as a result of fluid shear.

Therefore, the floc formation chamber is divided into several compartments (Figure 22 and 23) with decreasing velocity gradients (Figure 24).

In the first compartment the velocity gradient will be high (about 100 s⁻¹) and in the last compartment the velocity gradient will be low (about 5 s⁻¹). The optimal operation of the mixers must be determined empirically.

The flow opening between the compartments must be large enough to avoid local energy dissipation, as is the case in hydraulic flocculation (Figure 25).

Floc volume concentration



Figure 27 - Mixing device floc blanket installation at Berenplaat

WATER TREATMENT

WATER TREATMENT



Figure 28 - Mixing device flow blanket installation at Berenplaat

Further reading

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- Water treatment: Principles and design, MWH (2005), (ISBN 0 471 11018 3) (1948pgs)
- Unit processes in drinking water treatment, W. Masschelein (1992), (ISBN 0 8247 8678 5) (635 pgs)